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COLORATION OF SHALES IN BURNING

BY

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H. BATCHELOR 14 Apr 1937

I Introduction

The production of various color effects on brick in firing involves control of atmospheric conditions, both in the heating and cooling of the ware, and regulated temperatures or rates of temperature change. Much advancement has been made in industrial practice in production of a variety of colors and shades on face brick of both fire clay and shale. Less has been done in accurate study of the effects of various factors of firing and cooling conditions, as well as of body compositions, on the color development.

The process of producing various colors on clay ware by application of reducing conditions or with alternate reduction and oxidation treatment is termed "flashing." In industrial practice, the procedure varies considerably with different clays and products.

A common method of obtaining reducing conditions is by firing heavily with oil during the flashing period. The kiln temperature is allowed to drop 100°C. after 2" settle and the steam is cut down in the burners to allow just enough to atomize the oil. The oil produces a strongly reducing atmosphere which is maintained until the temperature again rises to the maximum, after which the kiln temperature is again allowed to drop 100° C. and the flashing is repeated. The number of flashes is determined by the appearance of samples which are drawn after each flash.

With coal firing, flashing is done first by cleaning the fires after 2" settle has been obtained; then building up a heavy fuel bed with fresh coal. The dampers during the flashing are almost completely closed. Heavy smoke issues from the stack. When this ceases, the fires are recharged and the operation continued

for about six hours, the length of time depending on the character of clay. After each firing and burning out, the kiln clears, at which time the controlling samples should be drawn. Some operators, instead of using the coal for reducing, introduce tar into the kiln through the crown hole of the kiln. This, however, produces bad discolorations in the region where the tar is introduced.

Gas-flashing follows the same procedure as with oil.

In cooling, kilns are usually kept closed tightly until the critical temperature is passed, after which they can be cooled in oxidizing conditions without loss of black color. By opening the kiln immediately after reduction, greens are produced; if too slow in cooling, browns to reds result from the excess reoxidation. To facilitate rapid cooling, large doors and roof vents are made with a method of blowing air into the bottom of the kiln. This was considered by Hull¹ as wasteful.

1. Review of literature.

² Seger, an early writer on coloration of brick, was of the opinion that the ferric oxide was reduced to the ferrous state, producing the black, and that the intermediate colors were a result of lacking quantity of iron. Color varied directly as the amount of iron present in the clay.

Flashing was a live problem with the American Ceramic Society from the time of the society's origin. Giessen³ introduced the subject, presenting two theories of flashing. First, a deposit of some sort on the brick produced the flash; second, a reduction of the ferric iron to ferrous iron produced the flash. He stated that the maximum burning temperature of the clay was the

necessary point at which to flash in order to produce permanent results. The statement that vitrified brick will not take a flash is disputable, as well as the statement that the flash is produced in cooling rather than during the actual reducing period.

⁴
Bleininger brought to attention the golds, greens, browns, and blacks producible by flashing of fire clay brick. Factors involved in flashing are chemical composition as a whole; amounts and character of iron; physical conditions of clay; temperature of burning; degree of reduction; and rate of cooling in relation to the rate of oxidation. He concludes that flashing is aided by lime and silicates; and that pyrite is highly desirable. His theory of coloration is based on the action of iron in porcelains. Immediately after reduction the color of the brick is gray with specks of ferrous silicates on it; upon cooling, the mass turns black.

⁵
Winchell describes only one silicate, Fe_2SiO_3 , as colorless, resembling the high-iron olivine, fayalite. The silicate is found in slags. ⁴
Bleininger further stated that iron oxide and silica cannot exist side by side and that their union is aided by fluxes. This would indicate the formation of a slag or glass such as was noted by Washington ⁶ in his study of Plateau Basalts. He tells of Fe_3O_4 forming as globules which decrease in size upon the increase in the glass content, forming a black glass which is very difficultly decolorized.

⁷
Felsner, in studying the coloration of glass by iron, found the following to be true,

2	parts	Fe_2O_3	and 3 parts of FeO	produces	blue glass
3	"	"	" 2 " " "	"	yellow glass
3	"	"	" 1 " " "	"	red "
1	"	"	" 6 " " "	"	black "

Full¹ stated that blacks are produced in strongly reducing kilns with rapid cooling; greens and browns are produced after the flash by cooling rapidly in oxidizing atmosphere; browns and blacks are produced by maintaining reducing conditions after flashing and cooling slowly. He also believes that coloration takes place in cooling.

Williams⁸ applied FeSO_4 ⁴ and FeCl_3 to the surface of a brick column with the following results,

- 1 Dry application gave no effect
- 2 Wet application was flashable and cured scumming.
- 3 FeCl_3 gave a better base for a flash
- 4 Scumming was overcome with FeCl_3 at much lower cost than with BaCO_3 ³

Lovejoy added the point that on dry-press brick, flashing was less effective than on stiff-mud brick due to the difference in densities.

Formation of iron silicates is very doubtful since only one is known, Fe_2SiO_4 , which is colorless, and further, no Fe-SiO_2 compounds were reported by Craig¹⁰ in his progress report on the study of the system $\text{FeO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$.

From the methods of firing we can readily conclude that a reduction of some sort takes place which is a chemical change. This change, according to literature, may be the reduction of

ferric iron to ferrous iron, the formation of silicates of iron and the formation of a black glass. The first and third theories are probable but--since only one iron silicate is known and it is colorless, and since no such compounds have been reported in a study of the system including such possibilities--we cannot include the second theory as possible in the coloration of shales. The chemical change is possible at high temperatures and may go either way, depending on the type of atmosphere and temperature. Therefore, in cooling, a critical temperature defines the limit above which the change will take place.

II Purpose and Plan of Studies

This paper takes up the study of colors produced in shale brick by manipulation of the atmosphere, the atmospheres necessary for the production of the different colors, and the microscopic structure of the variously colored brick, formulating a theory as to their existence.

Preliminary studies were made to determine the behavior of the clays to be studied in burning, the range of gas and air ratios within which reduction and coloration was possible, the proper type of furnace to use, the duration of flashing, and the temperature for flashing.

The possibilities in the reduction and oxidation atmospheres were summarized in the following outline.

I One reduction at the finishing temperature

A Rapid Cooling

- 1 Oxidizing conditions
- 2 Reducing conditions

B Slow cooling

1 Oxidizing conditions

2 Reducing conditions

II Two reductions at the finishing temperature

A Rapid cooling

1 Oxidizing conditions

2 Reducing conditions

B Slow cooling

1 Oxidizing conditions

2 Reducing conditions

Test pieces obtained by each of the above procedures were examined for color and structure, and representative samples were studied under the microscope.

III Materials Used

Six shales were chosen for the investigation.

1. Shale from the Alton Brick Company of Alton, Illinois which is of the paving brick type having a fair amount of carbon in it and no scumming salts.

2. Galesburg, Illinois shale which was very similar to shale number one.

3. Shale from the Streator Brick Company of Streator, Illinois which matured at a higher temperature than the two above, possessed considerably more carbon and some scumming salts.

4. Shale from the Danville Brick Company of Danville, Illinois which matured at a considerably lower temperature, containing very much carbon, and very little scumming salts.

5. Shale from the Coral Ridge Clay Products Company of

Coral Ridge, Kentucky which matured about midway between one and four, containing very little carbon, and a large amount of scumming salts.

3. Evansville, Indiana shale resembled the shale number five very closely except for the absence of scumming salts.

The iron content in all of these shales was about the same. The size of the iron oxide particles in the burned state varied but little in the different shales.

IV Preliminary Studies

1. Determination of safe firing temperature under oxidizing conditions.

Since flashing was to be done at the maximum temperature at which the clay could be safely fired and at lower temperatures, it was necessary to investigate the behavior of the clays at the different temperatures. To speed up the burning, the test pieces were previously oxidized to 900° C., the maximum oxidizing temperature of shales, before tests were made. Since Jackson's work was carried out with shales, his burning curve, which is found in graph 1, was adopted for this study. The results obtained in burning according to this curve are given in tables 1 and 2. It was found that clay number 4 was first to break down in structure at high temperatures with 5 and 6 showing lack of vitrification range. The maximum safe burning temperature for all the shales, which was used throughout the experimental work, was 1100° C.

Table 1

Study of maturing temperatures of clays

Clay	1	2	3	4	5	6
1050	soft	soft	soft	matured	matured	matured
1100	matured	matured	matured	overburned	matured	matured
$\frac{1}{2}$ Hr. 1100	glass	glassy	matured	glass	glass	glass
1 Hr. 1100	glass	glass	glass	glass	glass	glass

Table 2

Study of maturing temperatures of clays

Clay	1	2	3	4	5	6
Matured	1100	1100	$\frac{1}{2}$ Hr. at 1100	1050	1070	1070
Glassy	$\frac{1}{2}$ Hr. at 1100	1 Hr. at 1100	1 $\frac{1}{2}$ Hrs. at 1100	down at 1100	1100	1100

2. Determination of type of furnace.

Since control of the atmosphere was the object of the tests, it was necessary to adopt a furnace in which the regulation of atmospheric conditions would be independent of the heating burners. For this purpose, a muffle was placed in a surface combustion furnace. The six furnace burners heated the muffle while an auxiliary burner for control of atmospheric conditions was inserted in the muffle through a peep hole in the door. The thermocouple was introduced in the muffle through a hole in the back of the furnace and extended to the center of the muffle.

3. Determination of effect of various gas-air mixtures.

It was thought that a variation in the gas-air ratio of the mixture sent into the muffle for reducing was allowable. To find the limits of the range, gas was passed into the furnace alone. In each succeeding burn, an increased amount of air was mixed with the gas until a definitely oxidizing atmosphere was attained. It was found that a fairly wide range existed. The best results were obtained with a 1:3.77 gas-air ratio. A volume of 6.6 cubic feet of mixture per minute passing into the muffle of 1.5 cubic feet volume consisted of 1.75 cubic feet of gas and 4.85 cubic feet of air. Reduction was produced in a longer time with a mixture as low as 1:3.86. This shows that 40% to 60% of the required air for complete combustion is the allowable range with the best results obtainable using 42% of the air necessary for complete combustion.

An average analysis of the city gas of the Champaign-Urbana gas works used in the tests is as follows:

CO_2 and H_2S 3.8

C_2H_6	14.6
H_2	22.0
CH_4	17.0
H_2O	23.6
CO_2	1.0

Table 3 shows the analyses of the furnace gases at different times. These were made on a modified Orsat analyzer but no trace of hydrogen or any of the hydrocarbons was found. In the reducing flames, however, particles of carbon were present. These were deposited on the water of the collecting bottle. Gases were collected over a solution of zinc sulphate and sulphuric acid in water to prevent absorption of CO_2 by the water.

Table 3
Furnace Atmospheres

	Reduction during burning	Oxidation during burning	Reduction during cooling	Oxidation during cooling
CO_2	6.1	11.4	6.4	4.9
O_2	1.8	1.2	1.6	19.3
H_2	14.1	2.0	13.0	2.3
H_2O	75.6	87.4	77.0	80.5

Using less than 40% of the required air, the carbon deposition in the furnace was so heavy that a thin coating was deposited on the brick, preventing farther gas action and reduction. Using more than 80% of the required air, no reduction took place

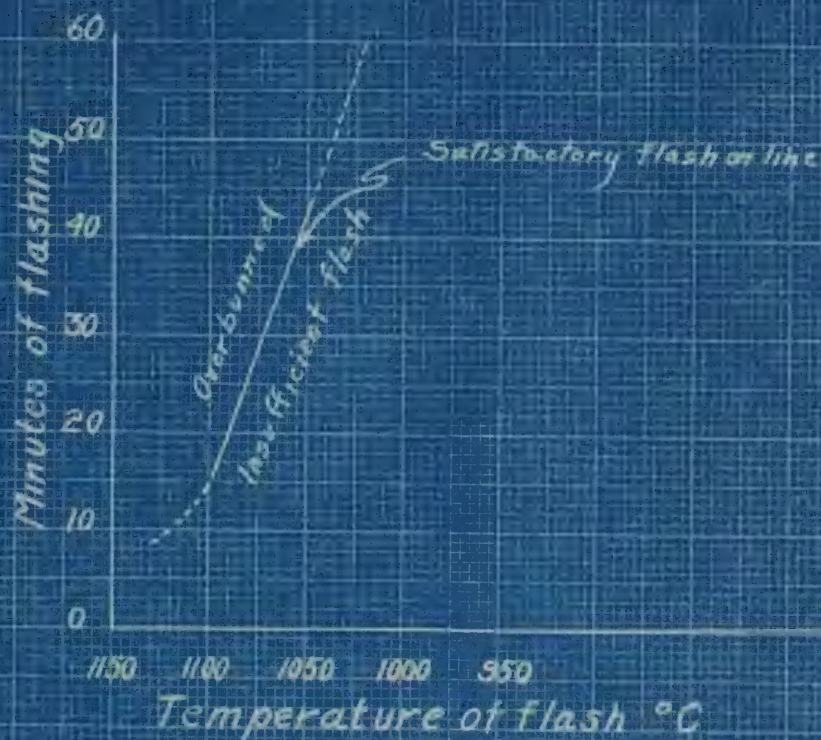
before brick structure failed.

4. Determination of effect of duration of reduction period.

Another possible variation in flashing was studied in the duration of the flash. Periods from five minutes to one hour were tried at the maximum temperature. Best results were obtained with a fifteen-minute flash. Less time was not sufficient and a longer period of reduction was detrimental to the structure of the brick, first producing too glassy a structure, followed by a vesicular structure.

5. Determination of safe firing temperature under reducing conditions.

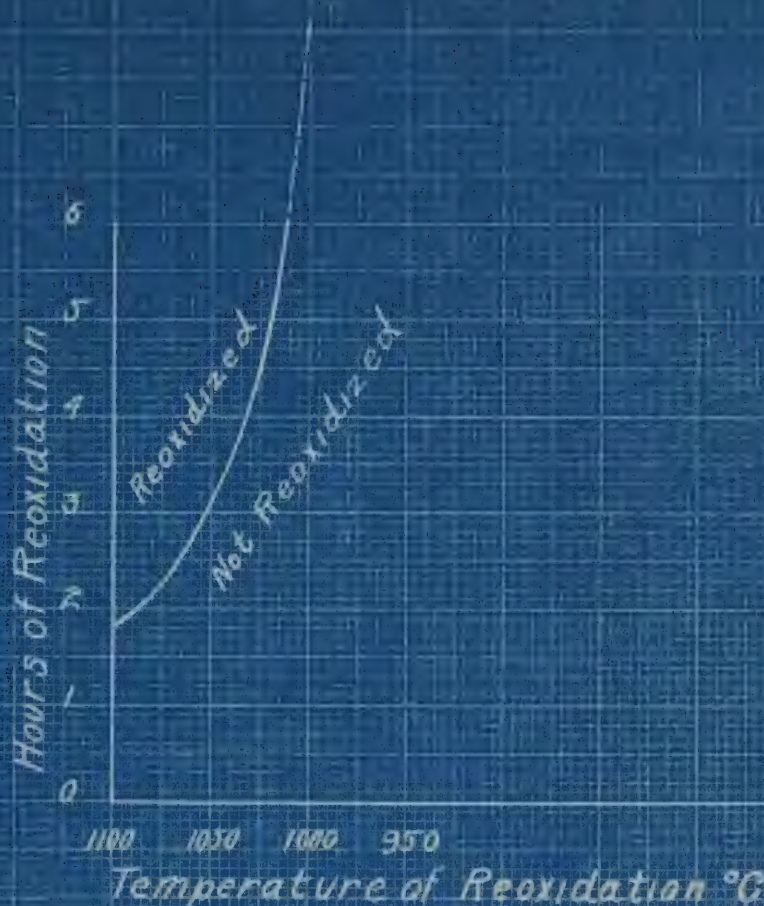
Flashes were made on the brick from 1150° C. to 1000° C. at 50° intervals. Samples were drawn during each flash and the flash continued until the samples resembled those from a fifteen minute flash at 1100° C. Flashing at higher temperatures than 1100° C. destroyed the structure. At lower temperatures an increased length of flashing period was required. Flashing was not effective or permanent below 1000° C. or the point at which the so called glass formation or sintering begins. This seems to have a definite bearing on the permanence of the flash. Graph 2 shows the relation of time and temperature in flashing.



Effect of Time and Temperature
in flashing

6. Determination of effect of various temperatures on rate of reoxidation.

After a fifteen minute flash at 1100° C. the furnace was quickly dropped to the desired temperature and held with a strongly oxidizing atmosphere until the samples showed reoxidation. Temperatures of reoxidation studied were 1100° , 1050° , 1000° . The rate of reoxidation was rapid at 1100° C., producing red colors in one hour and forty-five minutes. At 1050° degrees, red brick were obtained in a little over three hours. At 1000° degrees no evidence of reoxidation was noted after six hours of holding when the brick failed in structure. Graph three shows that cooling quickly below 1050° C. is a safe means of preserving dark colors and that slow cooling above this temperature will destroy the flash completely or produce various colors such as golds and greens.



Effect of Time and Temperature in Reoxidation

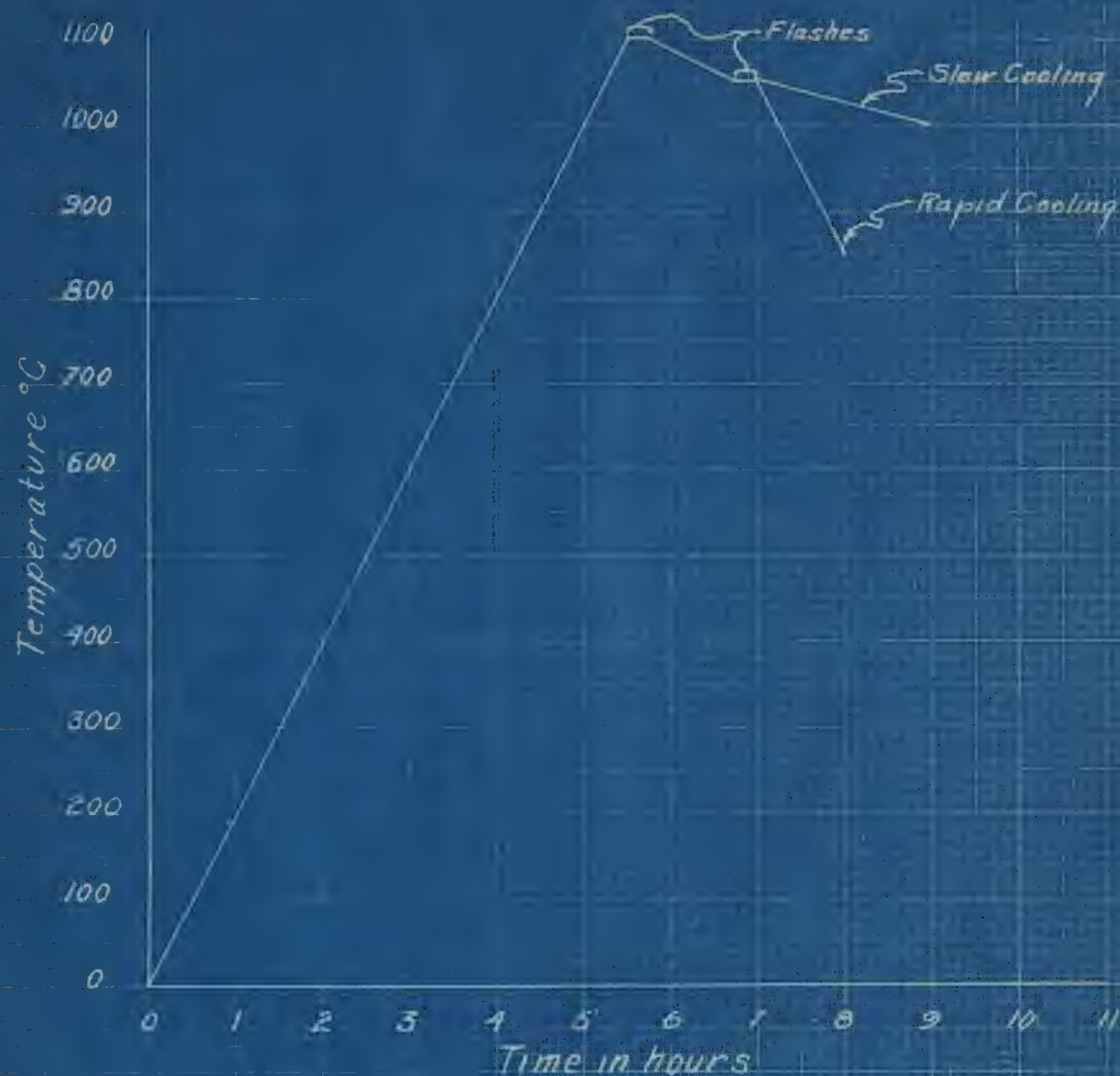
7. Summary of results of preliminary tests.

The preliminary test gave the following results which formed a basis for continuation of the flashing tests.

1. A rate of heating of 200° C. per hour was satisfactory.
2. The average maturing temperature of the clays was 1100° C.
3. The maximum safe flashing temperature was 1100° C.
4. Fifteen minutes at this temperature produced the best flashing results.
5. One hour at 1100° C. to three hours at 1050° C. was sufficiently slow cooling to produce reoxidation.
6. Less time than in No. 5 was sufficiently rapid cooling to prevent reoxidation.

V. Effect of flashing and cooling procedures on color.

In accordance with the results obtained in the preliminary tests, burning curves 4 and 5 were constructed to produce the variations which were required in the outline given under "Purpose and plan of study."



Burning Curves
Two Reductions

Graph 5

1. Experimental Procedure.

Briguettes were placed in the muffle with sufficient space between them to allow a good circulation of gases around each piece. The couple was so placed in the muffle that the hot junction was exactly in the center. The furnace was then heated to 1100° C. by six burners outside of the muffle preventing any action of these gases on the bricks. At 1100° C., the six burners were turned down so that to give about one half the gas supply used in the heating up period, an auxiliary burner, made of a porcelain, was introduced into the muffle through an opening in the door. The tube extended one third the length of the muffle into the muffle. Air and gas mixtures were introduced through this tube with sufficient velocity to blow to the rear of the muffle over the setting. The upper portion of the muffle was at higher pressure than the lower portion, therefore, reducing gases traveled back toward the door through the brick setting and were let out thru an opening in the bottom of the door of the muffle. For slow cooling in oxidation, the heating burners were kept at the same setting as during flashing and a stream of air was blown into the muffle. For rapid cooling in oxidation, a strong cold blast of air was blown into the muffle with all heating burners shut off. For slow, reducing cooling, the six outside burners were shut off and the muffle burner kept as during flashing. This burner supplied sufficient heat to follow the curve and maintain the reducing conditions. For rapid cooling in reduction, the bricks were transferred to a furnace kept under reducing conditions at a low red heat.

Since a second reduction at the maximum temperature destroyed the structure of the brick, it was necessary to reduce the tem-

perature of the second flash to overcome this. Therefore after the first flash the temperature was reduced to 1050 degrees centigrade in one hour and the second flash applied then after which the regular procedures of cooling were followed.

The following observations were made on the pieces:

1. Surface color
2. Surface structure
3. Interior color
4. Interior structure

Slides or thin sections of representative samples were made and examined. In some cases colorations were only surface effects and were too thin to permit making slides for study.

2. Results of tests.

One reduction and rapid cooling in oxidizing conditions, produced a dull black brick. One reduction and rapid cooling in reducing atmosphere produced also the same type of dull black color. Clays 1, 3, and 3, however, were olive green. This green color was a very thin skin effect due to probably the oxidation effect during the time it was being transferred thru the air to the cooling furnace. Slow cooling after one reduction in an oxidizing atmosphere showed definite signs of reoxidation, producing golds, yellows, reds, and browns. Slow cooling after one reduction in a reducing atmosphere, produced blacks. Due to an air current in the furnace, some of the faces were partially oxidized but the general color was a good dull black.

After two reductions and rapid cooling in oxidizing atmosphere, a brown-black color was produced. This indicates that the

additional heating produced a glassy structure which, after the oxidation between flashes, prevented a thorough flashing the second time. After two reductions and rapid cooling in a reducing atmosphere, the bricks were slightly darker than with the previous cooling. Slow cooling in oxidizing conditions after two reductions gave a deep brown red color. Slow cooling in reducing conditions after two reductions produced a black with a slight brown tint.

The results of the separate burns in this series of tests are shown in tables 4, 5, 6, and 7.

3. Summary of results.

Blacks were produced by rapid cooling in both oxidizing and reducing atmospheres; also by cooling in reducing atmosphere slowly. This indicates that they can be produced when no oxidation takes place or when cooling rapidly enough with oxidizing conditions through the active temperature range.

Complete reoxidation took place in an oxidizing atmosphere only in slow cooling, showing that this condition is necessary for the reaction.

Gold color was produced by reoxidation after one flashing, showing that such a color may result after a flashing treatment of moderate severity. In the case of slow oxidation following two reductions, the resulting color was a brown instead of the gold that resulted with similar cooling treatment after a single reduction.

Green was produced in the quickly cooled pieces under reducing conditions. Test pieces taken out of the furnace while under reducing conditions and carried thru the air to a furnace at

red heat and with reducing atmosphere developed green colors. This color is apparently a thin surface effect produced by rapid changes of alternating reducing and oxidizing conditions.

It will be noticed that after a second flash these color changes were very sluggish. The dark color produced by reduction was permanent. In the two-flash series, the surface of the bricks was glassy in every case, showing that this sintered, well-vitrified brick formed a coating that prevented the further action of gases on the minerals in the brick producing the color.

On long heating under oxidizing conditions, the brick formed the usual glass coating which was very thin and of a good chocolate-brown color.

Four outstanding results were noticed,

1. Reduction produced blacks.
2. Oxidation brought back the red or yellow colors.
3. Alternations of oxidizing and reducing conditions produced browns and greens and the intermediate colors.
4. Prolonged heating with oxidation produced browns.
5. After single reduction without formation of the thin glass coating on the brick, the color was easily acted upon by gases.
6. Reduced bricks with a thin glass coating acted sluggishly with respect to changes in color.
7. A glassy surface served as a protection to the reduced colorizing minerals in the brick, preventing action of gases on them and resultant change of colors.

Table 4

Study of Surface Colors

Clays Points	1	2	3	4	5	6
One reduction Rapid cooling Oxidizing conditions	Black	Black	Black	Black	Black	Black
One reduction Rapid cooling Reducing conditions	Olive Green Dirty orange to brown	Olive Green red brown	Olive Green dirty yellow green to black to gold	Black	Black	Black
One reduction Slow cooling Oxidizing conditions	Good black to green	Good black to green	green to black to gold	brown black green to black to gold	yellow to brown or gold	Black signs of good gold
One reduction Slow cooling Reducing conditions	Green Brown Black	Green Brown Black	gold Brown Black	Black	Black	Black to Green Brown Black
Two reductions Rapid cooling Oxidizing conditions	Black	Black	Black	Black	Black	Black
Two reductions Rapid cooling Reducing conditions	deep Brown red	deep Brown red	deep Brown red	deep Brown red	deep Brown red	deep Brown red
Two reductions Slow cooling Oxidizing conditions	Black	Black	Black	Black	Black	Black
Two reductions Slow cooling Reducing conditions	Black	Black	Black	Black	Black	Black

Table 5

Study of Surface Structure

vit= vitreous

Clay point	1	2	3	4	5	6
One reduction Rapid cooling Oxidizing conditions	vit	vit	vit	glassy	vit	vit
One reduction Rapid cooling Reducing conditions	vit	vit	vit	glassy	vit	vit
One reduction Slow cooling Oxidizing conditions	vit	vit	vit	glassy	vit	vit
One reduction Slow cooling Reducing conditions	vit	vit	vit	glassy	vit	vit
Two reductions Rapid cooling Oxidizing conditions	glassy	glassy	glassy	glassy	glassy	glassy
Two reductions Rapid cooling Reducing conditions	vit	vit	vit	vit	vit	vit
Two reductions Slow cooling Oxidizing conditions	glassy	glassy	glassy	glassy	glassy	glassy
Two reductions Slow cooling Reducing conditions	glassy	glassy	glassy	glassy	glassy	glassy

Table 6

Study of Interior color

Clay point	1	2	3	4	5	6
One reduction Rapid cooling Oxidizing conditions	red	red	red	red	red	red
One reduction Rapid cooling Reducing conditions	red	red	red	red	red	red
One reduction Slow cooling Oxidizing conditions	red	red	red	red	red	red
One reduction Slow cooling Reducing conditions	brown	brown	brown	brown	brown	brown
Two reductions Rapid cooling Oxidizing conditions	brown	brown	brown	brown	brown	brown
Two reductions Rapid cooling Reducing conditions	black	black	brown	brown	brown	brown
Two reductions Slow cooling Oxidizing conditions	Black	black	brown	brown	brown	brown
Two reductions Slow cooling Reducing conditions	black	black	black	black	black	black

Table 7

Study of Interior Structure

vit=vitreous

Clay point	1	2	3	4	5	6.
One reduction Rapid cooling Oxidizing conditions	vit	vit	vit	vit	vit	vit
One reduction Rapid cooling Reducing conditions	vit	vit	vit	vit	vit	vit
One reduction Slow cooling Oxidizing conditions	vit	vit	vit	vit	vit	vit
One reduction Slow cooling Reducing conditions	vit	vit	vit	vit	vit	vit
Two reductions Rapid cooling Oxidizing conditions	vit	vit	vit	glassy	glassy	glassy
Two reductions Rapid cooling Reducing conditions	glassy	glassy	glassy	glassy	glassy	glassy
Two reductions Slow cooling Oxidizing conditions	glassy	glassy	glassy	glassy	glassy	glassy
Two reductions Slow cooling Reducing conditions	glassy	glassy	glassy	glassy	glassy	glassy

VI Microscopic investigation.

1. Results

Shales, according to Harker¹² and Rogers,¹³ are made up of quartz, feldspar, kaolinite, decomposition traces of biotite, rarely zircon, epidote, limonite, siderite, calcite, magnetite, carbonaceous matter, pyrites, glauconite, rarely rutile, and hematite. Iron can therefore be contained in shales in biotite, epidote, limonite, siderite, pyrites, glauconite, and hematite.

The oxidized samples showed a definitely red color under the microscope. Hematite, Fe_2O_3 , which produced the color, occurred in large groups of particles and also scattered thruout the mass. The individual particles of hematite were 1 mu and larger in size with a tabular and irregular grain habit, appearing colorless under the high power.

The reduced samples showed the same tabular forms and grains but with the color changed to black. Pulverizing some of a reduced portion, and testing with a needle point under the microscope proved that these pieces were magnetic and therefore magnetite, Fe_3O_4 . The definite outline of the Fe_3O_4 was not changed in reduction, indicating that very little, if any, solution of iron in the glass occurs. No sign of iron silicates was noticed, although both iron and quartz were present in grain form. Since the only iron silicate known is colorless, we must strongly doubt Kleininger's statements in connection with his theory on colors in flashing.

2. Summary of results.

We may attempt to explain the cause of color in the following

way. If sections 1 mm in thickness were cut parallel to the face of the brick, each of the thin sections would contain quartz grains, black iron oxide grains, and a gray mass, commonly termed shale structure by petrographers. The black iron oxide is not evenly distributed. Therefore, if two thin sections are placed one on the other, the black particles in the one may or may not be above those of the lower section. The magnetite is seen only in the top section since the shale structure is not entirely transparent. The magnetite in the lower section, however, tends to darken the gray of the shale structure. Placing many such sections in a stack, the shale structure gradually darkens until a black is reached at a thickness of .05 mm. The number of particles reduced and the black color increase with increase of duration of flashing and the number of flashes. Looking at the face of a flashed brick, we are theoretically looking at many thin sections of reduced brick superimposed on each other, the resulting thickness depending on the depth of the flash. This coloration theory may also be used to explain the red and other colors produced in the bricks.

The intermediate colors, golds, browns, greens, etc., are produced by combinations of varying amounts of the different iron oxides. When the hematite predominates over the magnetite, the yellow color is prevalent. When the black oxide predominates over the hematite in amount, browns and the dark shades are produced. Fehner⁷ found the same in coloring glass with the two iron oxides. Bancroft¹⁴ states that varying size of particles causes variations in color, giving the example of Fe_2O_3 in large particles as red and in small particles as yellow. He adds that thickness of pigment layer varies the shade of color.

We may conclude from this that colors are due to the simple oxides magnetite and hematite. Particle size, relative amounts of each present, and thickness of pigment layer determines color.

VII General discussion of results.

Reduction produced a black color which was due to the reduction of hematite to magnetite. This material distributed heterogeneously in the reduced portion, gave the shale structure of the brick a black appearance, producing a dull black color.

Reoxidation restored the hematite from the magnetite producing again the reds and yellows. The distribution of the particles again was the cause of the red color. The variation in red to yellow was due to the size of hematite particles, the large ones giving a red and the small, a yellow color.

Partial reoxidation produced varying colors. Browns were the result of a short oxidation after reduction followed by reducing cooling. This color is due to a surface change of magnetite to hematite with the black background of magnetite. Browns were a result of reoxidation in slow cooling after two reductions. After two reductions, the brick has a slag coating which makes all chemical changes due to atmosphere manipulation difficult. Whereas, after one reduction a red or yellow is possible under these conditions, only a partial reoxidation takes place after two reductions, giving a brown. The brown color is due to a mixture of hematite and magnetite with the quantity of hematite slightly greater than that of the magnetite. Gold color results from a very great excess of hematite over magnetite.

After the development of the slag coating during the second

reduction, changes were very sluggish. Reoxidation of the blacks and reduction during this period produced brown tinted colors.

VIII Conclusions

1. Black is produced by rapid cooling after reduction to 1050° C. or slightly below, or by slow cooling in reducing conditions.
2. Golds are produced by partial reoxidation after flashing.
3. Browns are produced by short reoxidation above 1050° C. or by partial reduction of oxidized brick after a slag coating is formed.
4. Greens are produced by a short reoxidation at the maximum burning temperature followed by cooling in a reducing atmosphere. This is a surface effect.
5. It is most satisfactory to flash at the maximum burning temperature of the clay since the brick must be sintered or finished to hold the flash.
6. Permanence and intensity of color varies directly with time and temperature of flash.
7. Highly vitrified brick is difficult to flash and to reoxidize.
8. Reoxidation is not materially effective below 1250° C.
9. Black color is due to magnetite.
10. Red color is due to hematite.
11. Gold color is due to hematite being present in much greater quantities than magnetite.
12. Brown color is due to a slight excess of hematite

present over magnetite.

13. Green is due to surface reoxidation to hematite with a black magnetite background.

14. Color, in general, is due to hematite and magnetite in varying amounts of each, size of particles, and thickness of pigment layer.


IX Acknowledgement

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